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PREPARATION OF PHENYL ARYL SULFIDES BY REACTION OF BENZYNE WITH ETHYL ARYL SULFIDES

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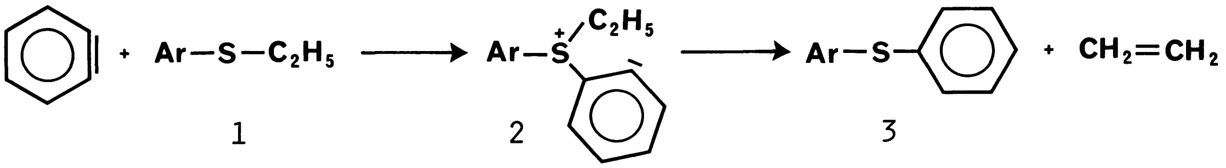
A variety of ethyl aryl sulfides (**1**) react with benzyne, with evolution of ethylene, to give phenyl aryl sulfides (**3**) in excellent yields, thus providing a general synthesis of **3** from arenethiols since **1** are quantitatively obtainable from arenethiols and ethyl bromide.

Reactions of sulfides with benzyne give betaines as initial products, which then decompose in several modes of reactions to give final products. Elimination of olefins yielding another sulfides is one of predominant reactions, when the substituent on sulfur possesses a β-hydrogen.[1)] We now found that betaines (**2**), produced by reactions of ethyl aryl sulfides (**1**) with benzyne, decompose, with evolution of ethylene, to give excellent yields of phenyl aryl sulfides (**3**)[2)] as the sole products, thus providing an efficient synthesis of **3** from arenethiols since **1** are quantitatively obtainable from arenethiols and ethyl bromide.[3)]


1 2 3

Aprotic diazotization of anthranilic acid followed by thermolysis of the resulting benzenediazonium-2-carboxylate was chosen as a source of benzyne.[4)] The reaction was done by adding a solution of anthranilic acid in dioxane to a refluxing mixture of an ethyl aryl sulfide **1** and isoamyl nitrite in 1,2-dichloroethane. An excess of anthranilic acid (benzyne, 2 mol. equiv.) was employed in order to obtain an optimized yield of **3** with 100% consumption of **1**.[5)] Results summarized in the Table show the usefulness of the method; yields are excellent without any exception. The reaction is also applicable to the conversion of *o*-bis(ethylthio)benzene (**4**) to *o*-bis(phenylthio)benzene (**5**). The reaction carried out by using 4 mol. equiv. of anthranilic acid gave **5**[2g)] (bp, 170 °C/1 mmHg) in 90.5% yield.

The following represents a general procedure. To a gently refluxing solution of an ethyl aryl sulfide (10 mmol) and isoamyl nitrite (21 mmol) in 1,2-dichloroethane (80 ml) was added dropwise a solution of anthranilic acid (20 mmol)[5)] in dioxane (10 ml) over a period of 15 min. After completion of the addition, the mixture was refluxed for 30 min. The resulting orange to red mixture was evaporated under reduced pressure, and the oily residue was passed through a short silica gel column (Merck, Art 7734, 40 g, hexane as eluent) and then distilled or recrystallized to give **3**.

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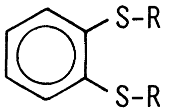
Table Preparation of Phenyl Aryl Sulfides **3**[a]

Ar	yield (%)[b]	bp (°C/mmHg)[c]	Ar	yield (%)[b]	bp (°C/mmHg)[c]
C_6H_5	92	105/1	p-BrC_6H_4	96	125/0.5
o-MeC_6H_4	96	110/0.6	p-MeOC_6H_4	87	137/0.7
m-MeC_6H_4	93	120/1.2	2,4,6-$Me_3C_6H_2$	90[e]	115/0.25
p-MeC_6H_4	95	123/1.1	1-naphthyl	90	(mp 41.5-42 °C)
p-$Bu^tC_6H_4$[d]	93	140/1.3	2-naphthyl	92	(mp 49.5-50.5 °C)
p-ClC_6H_4	97	125/1			

[a] All of **3** except phenyl p-(tert-butyl)phenyl sulfide are known compounds. [b] Yields based on isolated pure products. [c] Pot-to-pot distillation (Kugelrohr). [d] ^{1}H NMR δ ($CDCl_3$) 1.30 (s, 9H) and 7.2-7.4 (m, 9H). [e] Three mol. equiv. of anthranilic acid was required since ethyl mesityl sulfide is less reactive toward benzyne because of steric hindrance (the reaction with 2 mol. equiv. of anthranilic acid gave phenyl mesityl sulfide in 75% yield with 20% recovery of the starting sulfide).



4 : R = Et
5 : R = Ph

References

1) R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, 1967, p. 164.

2) For representative preparation of diaryl sulfides, see a) J. F. Bunnett and T. K. Brotherton, J. Org. Chem., 23, 904 (1958); b) J. R. Campbell, J. Org. Chem., 29, 1830 (1964); c) T. Fujisawa, T. Kobori, N. Otsuka, and G. Tsuchihashi, Tetrahedron Lett., 5071 (1968); d) J. F. Bunnett and X. Creary, J. Org. Chem., 39, 3173 (1974); e) T. Migita, T. Shimizu, Y. Asami, J. Shiobara, Y. Kato, and M. Kosugi, Bull. Chem. Soc. Jpn., 53, 1385 (1980); f) F. Bottino, R. Fradullo, and S. Pappalardo, J. Org. Chem., 46, 2793 (1981); g) H. J. Cristau, B. Chabaud, A. Chêne, and H. Christol, Synthesis, 829 (1981); h) P. Jacob III and A. T. Schulgin, Synth. Commun., 11, 957 (1981); i) R. B. Bates and K. D. Janda, J. Org. Chem., 47, 4375 (1982).

3) Ethyl aryl sulfides **1** are conveniently prepared as follows: to a stirred mixture of 50 mmol of an arenethiol, ca. 0.5 g of trioctylmethylammonium chloride (phase transfer catalyst), and 55 mmol of KOH in 20 ml of water was added 55 mmol of ethyl bromide in one portion, and stirring was continued for ca. 1 h. Usual workup of the mixture gave **1** nearly quantitatively.

4) F. M. Logullo, A. H. Seitz, and L. Friedman, Org. Synth., 48, 12 (1968).

5) A varied amount of anthranilic acid was used in the reaction with ethyl phenyl sulfide, which showed that the use of 2 mol. equiv. of anthranilic acid was required to obtain an optimized yield of diphenyl sulfide with 100% conversion of the starting sulfide.

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